



Facile synthesis of acyl chitosan isothiocyanates and their application to porphyrin-appended chitosan derivative



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ABSTRACT

Chitosan (**1**) was reacted with phenylisothiocyanate in 5% AcOH/H₂O to give *N*-phenylthiocarbamoyl chitosan (**2**) with a degree of substitution (DS) of *N*-phenylthiocarbamoyl groups of 0.86 in 87.1% yield. The following acylation of compound **2** with hexanoyl chloride in the presence of pyridine afforded 3,6-di-*O*-2,3-hexanoyl chitosan isothiocyanate (**4a**) with a DS of the isothiocyanate groups of 0.70 in high yield, unexpectedly. Compound **4a** exhibited high levels of reactivity toward various amines to give the corresponding *N*-thiocarbamoyl chitosan derivatives in high yields. Other acyl (decanoyl (**4b**), myristoyl (**4c**), stearoyl (**4d**), benzoyl (**4e**)) chitosan isothiocyanates were also prepared from chitosan (**1**) in high yields. To evaluate the potential applications of acyl chitosan isothiocyanates, *N*-(triphenylporphyrinyl)thiocarbamoyl chitosan derivative **6** with a DS of the triphenylporphyrinyl groups of 0.46 was prepared from compound **4b**. The Langmuir–Blodgett monolayer film of compound **6** gave a good photon-to-electron conversion performance.

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1. Introduction

Chitosan is a linear cationic heteropolymer of *N*-acetylglucosamine (GlcNAc) and glucosamine (GlcN) residues thorough β -1,4 linkages by the deacetylation of chitin which is the second most abundant natural biopolymer in nature, and a most versatile polysaccharide that lends itself to countless chemical and biochemical modifications (Harish Prashanth & Tharanathan, 2007; Kurita, 2006; Mouya & Inamdar, 2008; Muzzarelli & Muzarelli, 2005; Muzzarelli, Tosi, Francescangeli & Muzzarelli 2003; Ravi Kumar, Muzzarelli, Muzzarelli, Sashiwa, & Domb, 2004; Rinaudo, 2006; Sahoo, Sahoo, Mohanty, Sasmal, & Nayak, 2009). However, considerable levels of attention have still been focused on the development of the high-value-added utilization for chitosan and its derivatives.

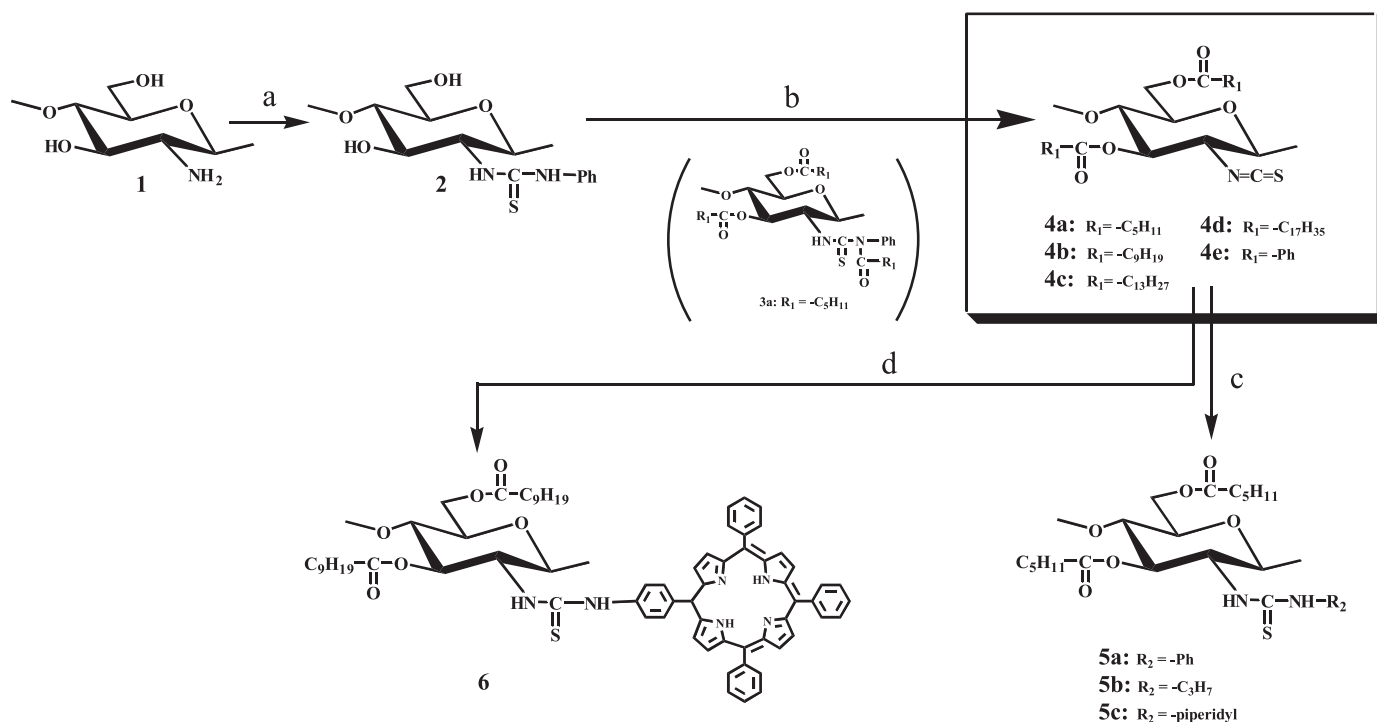
The *N*-substituted thiocarbamoyl chitosan derivatives which was prepared by *N*-thiocarbamoylation of chitosan with isothiocyanate compounds are one of the important functional chitosan derivatives. For example, *N*-acetyl- (Fekry & Mohamed, 2010), *N*-acyl- (Zhong et al., 2008), *N*-fluoresceinyl- (Ma et al., 2008; Qaqish

& Amiji, 1999), *N*-phenyl- (Baba, Noma, Nakayama & Matsushita, 2002, Monier & Abdel-Latif, 2012) thiocarbamoyl chitosan derivatives has been reported as a corrosion inhibitor, an antimicrobial material, a macromolecular fluorophore, a metal adsorbent, respectively. However, the availability of the commercial isothiocyanate compounds are limited. If chitosan isothiocyanate derivatives are easily synthesized, various amines are available for the syntheses of versatile *N*-substituted thiocarbamoyl chitosan derivatives for new applications. Glucosamine isothiocyanate derivatives can be prepared by the reaction of glucosamine with thiophosgene (Fernández-Bolaños, Zafra, López, Robina & Fuentes, 1999; Jochims & Seegler, 1965), but similar chitosan isothiocyanate derivatives have not been reported in the literature, even though chitosan has an amino group at its C-2 position that could be converted to an isothiocyanate group. The isothiocyanation of amines can be achieved by the reaction of an amine with thiophosgene or carbon disulfide (Fernández & Mellet, 1999, Munch, Hansen, Pittelkow, Christensen & Boas, 2008; Mukerjee & Ashare, 1991; Sun, Hu, Zhao, & Liu, 2012; Sun, Li, et al., 2012), although it is important to mention that both of these reagents are highly toxic. With this in mind, the development of a facile and safe synthetic method for the formation of chitosan isothiocyanate derivatives is strongly desired.

We recently reported a facile and safe synthetic method for acyl chitosan isothiocyanates by two reactions, that is, *N*-phenylthiocarbamoylation with phenylisothiocyanate and

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- a) Ph-N=C=S/ 5%-AcOH/H₂O/ MeOH, 30°C, 48 h ; b) Acyl chloride/ Pyridine / CHCl₃, 1°C, 1 h → 30°C, 1 h → 80°C, 18 h
 c) Amine/ THF, 35°C, 48 h; d) TPP-NH₂/ CH₂Cl₂, 35°C, 48 h

Scheme 1. Preparation of *N*-substituted thiocarbamoyl chitosan derivatives (**5a–c** and **6**) via the corresponding acyl chitosan isothiocyanates (**4a–e**).

acylation with acyl halide or acyl anhydride (Takano & Shibano, 2013). The resulting acyl chitosan isothiocyanates are soluble in common organic solvents and are expected to be useful synthetic intermediates for new functional chitosan derivatives. But, we did not report this procedure in its full detail.

On the other hand, the synthesis of porphyrin-containing chitosan derivatives represents one of several recent proposals for the high-value-added utilization of chitosan, with other examples including the construction of metallotetraphenylporphyrin appended chitosan derivatives (Huang, Guo & Tang, 2007), the use of an Mn(III) deuteroporphyrin-bearing chitosan as catalyst for oxidation reactions (Sun, Hu, et al., 2012), and tetraphenylporphyrin tethered chitosan derivatives for use as nanocarriers for gene delivery (Gaware et al., 2013). The LB monolayer films of 6-*O*-porphyrinyl-2,3-di-*O*-stearoyl cellulose, which is a regioselectively substituted cellulose derivative, have been reported to exhibit high photon-to-electron conversion performances (Sakakibara, Ogawa & Nakatsubo, 2007). The high performance of this material has been attributed to the dense packing of the porphyrin moieties along the cellulose backbone because of the well-defined and regular structure of the cellulose derivative. The *N*-porphyrinylthiocarbamoyl chitosan derivatives prepared from the acyl chitosan isothiocyanates could therefore potentially be used as alternative photon-to-electron conversion materials.

This paper provides a detailed account of our new method for the synthesis of acyl chitosan isothiocyanates (Scheme 1). Furthermore, we have described the reactivity of these materials with various amines, and the preparation and evaluation of an LB monolayer film of porphyrin-appended chitosan derivative as one of the examples of the application of the isothiocyanates for the preparation of functional chitosan derivatives.

2. Experimental

2.1. General

Chitosan (DAICHITOSAN 100D (VL), degree of deacetylation 98%) was kindly supplied by Dainichiseika Color & Chemicals Manufacturing Co. (Tokyo, Japan). All of the other chemicals used in the study were purchased from commercial sources and used without further purification. Fourier-transform-infrared (FT-IR) spectra were recorded on a Shimadzu IR Prestige-21 spectrophotometer (Shimadzu, Kyoto, Japan) as KBr pellets (sample 1 mg/KBr 200 mg). ¹H and ¹³C NMR were recorded on a Varian 500 MHz FT-NMR spectrophotometer (Agilent Technologies, Santa Clara, CA, USA) using tetramethylsilane (TMS) as an internal reference standard in DMSO-*d*₆ or CDCl₃. The standard number of scans in the ¹H and ¹³C NMR measurements were 3500 and 22,000, respectively. The chemical shifts (δ) of the NMR spectra have been reported in parts per million (ppm). UV–vis spectra were recorded on a Jasco V-560 UV–vis spectrophotometer (Jasco, Tokyo, Japan).

2.2. Preparation of acyl chitosan isothiocyanate

2.2.1. *N*-Phenylthiocarbamoylation

Chitosan (**1**, 1.20 g, 7.45 mmol) was dissolved in a 5% (v/v) solution of AcOH in water (30 mL) and the resulting solution was diluted with MeOH (120 mL). Phenyl isothiocyanate (5.34 mL, 44.7 mmol) was then added to the solution, and the resulting mixture was stirred at 35 °C for 24 h, during which time a precipitate formed. The precipitate was filtered, and the filter-cake was washed with MeOH before being collected and suspended in MeOH (300 mL) without drying. The suspension was then stirred at ambient temperature for 30 min and filtered, and the filter-cake was washed with MeOH. This purification procedure was repeated several times until no

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